

Laboratory Name: LLNL
B&R Code: KC020101

FWP and possible subtask under FWP:

Complex Transient Events in Materials Studied Using Ultrafast Probes and Terascale Simulation

FWP Number:

SCW0289

Program Scope:

We seek to study complex transient phenomena by applying ultrafast techniques to observe material processes. The new technique of dynamic transmission electron microscopy (DTEM) has been identified as a potentially powerful technique to characterize the evolution and identify mechanisms in fast, dynamic events in materials. We plan to explore the atomic level mechanisms and structures in martensitic transformations in materials, specifically the pressure driven α to ϵ transformation in Fe and the temperature driven α to β transformation in Ti (and related systems, e.g. Zr, Hf). We also plan to study phase nucleation and evolution in rapid solid-state chemical reactions in the reaction front of self propagating reactive multilayer thin films.

Major Program Achievements (over duration of support):

We have achieved routine operation of the DTEM at LLNL for the conditions of 10 ns pulsed electron beam operation with 3×10^7 electrons per pulse. Transient states are initiated in the specimen by optically pumping it with a laser. This treatment laser has a pulse duration of 12 ns FWHM and energies up to several mJ per pulse. We have used specimen drive pulses of a few μ J to heat specimens of Ti into the β phase field and quantify their structural transformation as a function of time with pulsed, selected area electron diffraction. We have used these data to construct the first isothermal time-temperature-transformation diagram with nanosecond time resolution. These data have been fit to a model of martensite growth, through which we have calculated temperature dependent activation energies for the transformation. We have also demonstrated dynamical image contrast formation in the DTEM for the first time and we have demonstrated a spatial resolution of approximately 20 nm in single shot imaging mode.

Program impact:

We have commissioned an instrument that can perform electron diffraction and imaging experiments of TEM specimens being irradiated with a treatment laser with high spatial resolution of 20 nm and on the time scale of 10 ns. This is the highest combination of spatial and temporal resolution ever achieved with any characterization technique. We have also reached out to the academic community, forming collaborations with several investigators (see below) on high impact areas of study.

Interactions:

Prof. Jorg Wiezorek, U. Pitt. - Solidification in confined metal layers.

Prof. Eric Stach, Purdue University – in-situ indentation for dislocation dynamics experiments.

Prof. Andreas Schroeder, UIC – Using RF cavities for electron pulse compression in DTEM.

Prof. John Spence, ASU – New laser stimulated field emission source of electrons for high time resolution.

Prof. Judith Yang, U. Pitt. – Time evolution of the early stages of corrosion at surfaces.

Recognitions, Honors and Awards (partly attributable to support under this FWP or subtask):

Invited presentation for Dr. G.H. Campbell, at M&M 2006 in Chicago, IL, on Aug. 2, 2006, “Applying the dynamic transmission electron microscope to study fast processes in materials.”

Invited presentation for Dr. G.H. Campbell, at the Gordon Research Conference on Physical Metallurgy, Holderness School, Plymouth, NH, July 24, 2006, “Using Nanosecond Transmission Electron Microscope to Study Solid-Solid Phase Transformations in Materials”.

Invited presentation for Dr. G.H. Campbell, at the MRS Fall Meeting 2006 in Boston, MA, on Nov. 29, 2006, “Nanosecond microscopy of hard and soft materials with the dynamic transmission electron microscope.”

Invited presentation for Dr. T. LaGrange at Swiss Institute of Technology in Lausanne (EPFL), June 9, 2006, “Nanosecond Dynamic Transmission Electron Microscope”.

Invited presentation for Dr. T. LaGrange at Rutgers University, Piscataway, NJ, November 14, 2006, “Nanosecond Dynamic Transmission Electron Microscope: studying ultrafast phenomena materials”.

Personnel Commitments for FY2007 to Nearest +/- 10%:

Dr. G.H. Campbell (PI) (30%), Dr. T.B. Lagrange (staff) (100%), Ms. J.S. Kim (student) (100% time on this project, however her effort is supported by a LLNL SEGRF scholarship).

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA \$274k

FY05 BA \$359k

FY06 BA \$352k

Laboratory Name: Lawrence Livermore Nat. Lab.
B&R Code: KC020102

FWP and possible subtask under FWP:

Microstructural evolution and mechanical response of complex alloys under prolonged particle radiation

FWP Number: SCW0343

Program Scope:

New theoretical developments to firmly establish the physical basis of multi-field, quantitative Phase-Field Method for simulations of microstructure evolution in irradiated materials. New computational algorithms for solving efficiently the Phase-Field and related kinetic models. Experiments and atomistic calculations for both calibrating the model parameters relevant to specific alloys and testing key predictions such as the onset of microstructural instabilities under irradiation.

Major Program Achievements (over duration of support):

Real-space Phase-Field microstructure simulator: Developed a new real-space implementation of the Phase-Field method with full account of micro-elasticity. The new real-space algorithm is exactly equivalent to the traditional Phase-Field approaches (based on reciprocal Fourier space) but is potentially much more efficient and allows for multi-scale simulations of materials with complex microstructure.

New first-passage Monte Carlo approach: Developed a novel algorithm for diffusion Monte Carlo simulations based on the theory of first passage processes applicable in any spatial dimension (1D, 2D, 3D, etc) and allowing for simulations covering an extremely wide range of time scales (from picoseconds to years).

Program Impact:

Based on the new real-space implementation, the new Phase-field code is under development that will be used for accurate simulations of microstructure evolutions in materials subjected to prolonged irradiation. For this, the new real-space Phase-Field capability will be combined with the multi-field Phase-Field model under development in UIUC.

The new diffusion Monte Carlo code allows efficient simulations of defect microstructure including nucleation and ripening of defect clusters directly from the underlying atomistic processes (diffusion, coalescence, annihilation, etc). This new capability will be used to understand conditions under which the model alloys will become unstable under prolonged irradiation.

Interactions:

UIUC (R. Averback, P. Bellon and I. Robertson)
Stanford University (W. Cai)
Carnegie Mellon University (A. Acharya)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

American Physical Society Fellowship to V. V. Bulatov
Edward Teller Fellowship to V. V. Bulatov

Personnel Commitments for FY2005 to Nearest +/-10%:

V. Bulatov (50%)
G. Gilmer (30%)

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA \$0

FY05 BA \$300k

FY06 BA \$294k

FWP and/or subtask Title under FWP: SCW0687

Understanding Molecular Hydrogen Absorbents: A First Principles Theory for van der Waals Interactions

FWP Number: SCW0289

Program Scope:

In this program we are developing accurate and efficient methods for using first-principles calculations to predict weak binding energies, such as van der Waals (vdW) interactions in materials. We are developing modifications to the widely used local density functional theory to include explicitly the non-local correlation effects particularly tailored for vdW interactions. In implementing our approach, we are utilizing linear scaling Quantum Monte Carlo methods to accurately determine the contribution of correlation energies to the total energies of electron systems. These methods will be generally applicable to a wide range of systems whose properties depend on weak binding, such as vdW solids, or biological molecules that interact via hydrogen bonds. However, we will initially focus on studying systems for storing molecular hydrogen via physisorption onto surfaces. These calculations will be used to evaluate candidate materials for storing hydrogen for use on fuel cell powered vehicles.

Major Program Achievements (over duration of support):

We have performed a series of benchmark calculations of the binding energy of molecular hydrogen to prototype storage materials. These calculations were performed using the linear scaling, fixed node, diffusion Quantum Monte Carlo (QMC) developed at LLNL. As a prototype for carbon-based storage materials we selected the C_{36} fullerene molecule. First, this QMC approach was compared with state-of-the-art, high-level quantum chemistry (coupled cluster) calculations for H_2 binding to a similar system, in this case, to the BH_3 molecule. These calculations demonstrated that QMC can predict these weak binding energies to within 0.02 eV/ H_2 . This is a significant result, as quantum chemistry calculations can currently handle systems with only a handful of electrons, but the QMC, on the other hand, can efficiently model systems with at least several hundred electrons.

We then studied a series of doped C_{36} molecules to find those with the highest binding energies. Boron doped C_{36} was found to have a binding energy closest to the desired value of 0.3 eV/ H_2 for on-board vehicular storage. For this $C_{35}B$ system, a Density Functional Theory calculation using the LDA functional yields an H_2 binding energy of 0.39 eV/ H_2 , whereas the gradient corrected GGA functional predicts, instead, an H_2 repulsion, -0.03 eV/ H_2 . While numerous experimental studies on weakly bounded systems have often suggested that LDA typically overestimates whereas GGA typically underestimates the binding energies, it had been impossible to theoretically quantify such weak interactions until this QMC work, which predicted 0.2-0.05 eV/ H_2 for the $C_{35}B-H_2$ system. These benchmark QMC studies of hydrogen interactions were published in Physical Review Letters.

Program Impact:

The methods developing in this project will have a broad impact in computational materials science. They will enable more accurate and efficient calculations of systems ranging from biological molecules to hydrogen storage materials.

The specific application of these techniques to physisorption hydrogen storage materials will help to establish the scientific base for the DOE/EERE go/no go decision on the use of molecular absorbents by FY09.

Interactions:

National Renewable Energy Laboratory (Dr. Shengbai Zhang, Dr. Yong-Hyun Kim)
University of Cambridge, U.K. (Prof. Richard Needs, Dr. Michael Towler)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

3 Invited talks (DOE Hydrogen Program Reviews, MRS, Santa Barbara Hydrogen Storage Workshop)

Publications:

Y.-H. Kim, Y. Zhao, A.J. Williamson, M. Heben, and S. Zhang, *Non-dissociative adsorption of H_2 molecules in light-element-doped fullerenes*, Physical Review Letters 96, 016102 (2005).

Personnel Commitments for FY2007 to Nearest +/-10%:

Dr. Andrew Williamson (2 months)

Dr. Sebastien Hamel (6 months)

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA \$0

FY05 BA \$0

FY06 BA \$150k

FWP and/or subtask Title under FWP: SCW0289

Ab initio Design of Nanomaterials with Pressure: The Search for Novel Materials

FWP Number: SCW0289

Program Scope:

In this program, we are using first-principles electronic structure simulations to investigate the use of pressure to control the properties of materials at the nanoscale. Recent experiments have shown that the response of nanomaterials to pressure can be dramatically different to that of their bulk counterparts. Nanomaterials have different bulk moduli and deformation potentials to their bulk counterparts. They behave as single structural domains that change shape during solid-solid phase transitions and exhibit transition kinetics dominated by size dependent single nucleation events. We are combining our recently developed capabilities for modeling nanoscale materials and materials under pressure to examine nanoscale materials under pressure, composite nanomaterials with built-in pressure, and the phase diagrams of nanoparticle arrays. These simulations will be used to explore new properties and structural phases of nanomaterials, which can be accessed by applying pressure and in some cases locked-in by constructing composite nanomaterials. Through this systematic process, we will separately engineer nanomaterials building blocks with novel, pressure-induced properties, and design the composite nanomaterials with technologically desirable material properties.

Major Program Achievements (over duration of support):

In the first phase of this project, we have focused on studying complex nanomaterials heterostructures with built-in pressure. We have examined the properties of silicon quantum dots embedded in amorphous silicon nitride matrices and silicon nanowires with a range of different surface structures and surface chemistries. These studies revealed that it is possible to engineer the opto-electronic properties of semiconductors at the nanoscale by applying pressure via a lattice mismatched embedding matrix material or by reconstructing the surfaces and interfaces of the material to apply pressure to the nanomaterials core. These results have led to exciting predictions for how to manufacture electrically pumped lasers, directly integrated on a silicon chip. They have also predicted that silicon nanowires exhibit an anomalously high Young's modulus and an anomalously low electron effective mass. These properties make silicon nanowires attractive candidates for high frequency mechanical resonators and microelectronic devices.

Program Impact:

This systematic theoretical exploration of pressure, in connection with experiments carried out both at LLNL and ORNL, promises to unveil both new materials and novel basic physical properties of materials at the nanoscale.

Interactions:

Oakridge National Laboratory (Dr. Fernando Reboredo)
Massachusetts Institute of Technology (Prof. Nicola Marzari, Prof. Lionel Kimerling)
Boston University (Prof. Luca dal Negro)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Invited talks: MRS, APS, ACS

L. Dal Negro, S. Hamel, N. Zaitseva, J.H. Yi, A.J. Williamson, G. Galli, and L.C. Kimerling, *Synthesis, Characterization and Modeling of Colloidal and Thin Film Silicon Nanocrystals*, IEEE Nano Photonics, (2006).
T. Vo, A.J. Williamson, and G. Galli, *First Principles Simulations of the Structural and Electronic Properties of Silicon Nanowires*, Physical Review B, 74 045116 (2006).
L. Dal Negro, J.H. Yi, L.C. Kimerling, S. Hamel, A.J. Williamson, and G. Galli, *Light emission from silicon-rich nitride nanostructures*, Applied Physics Letters 88, 183103 (2006).
N. Drummond, A.J. Williamson, R.J. Needs and Giulia Galli, *Electron emission from diamondoids: A diffusion quantum Monte Carlo study*, Physical Review Letters 95, 096801 (2005).

Personnel Commitments for FY2007 to Nearest +/-10%:

Dr. Andrew Williamson (3 months)
Dr. Tadashi Ogitsu (2 months)
Dr. Byeongchan Lee (2 months)

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA \$0

FY05 BA \$0

FY06 BA \$350k

Laboratory Name: Lawrence Livermore National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:

Virus assembly at nanoscale chemical templates

FWP Number: SCW0289

Program Scope:

The purpose of this research is to use templated deposition of engineered viruses as a way of investigating the physics that controls directed organization of complex biomolecules at surfaces. Site-specific engineering of viral proteins, synthesis of chemoselective linker molecules, and nanoscale patterning of those linkers will be used to create the viral arrays. Chemical force, confocal, and atomic force microscopy will be employed to characterize virus-virus and virus-substrate interactions, the kinetics of early aggregation events, and the morphology of assembly, respectively. Molecular dynamics and kinetic Monte Carlo simulations will be compared to the experimental results in order to build a physical picture of the aggregation and assembly process. This research is motivated by the potential of viruses arrays as vehicles for creating predefined micron-scale patterns of functional molecules and materials which are in turn organized at the molecular level by the viral template.

Major Program Achievements (over duration of support):

N/A (New project start, July FY06)

Program Impact: Has created focused effort to develop capability in and physical understanding of directed assembly of large macromolecular complexes at surfaces. Has enabled collaboration between interdisciplinary group of biologists, chemists, physicists and materials scientists at three major universities and multiple groups within the Biosecurity and Nanosciences Laboratory at LLNL.

Interactions:

Internal—Computational Materials Sciences Group; Molecular imaging, Nanophotonics, and Molecular biophysics and functional nanostructures Groups within the Biosecurity and Nanosciences Laboratory, LLNL

External—Department of Materials Science and Engineering and Department of Biological Engineering, Massachusetts Institute of Technology; Department of Molecular Biology, The Scripps Research Institute; Department of Chemistry, University of California at Berkeley.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

N/A (New project start, July FY06)

Personnel Commitments for FY2005 to Nearest +/- 10%:

N/A (New project start, July FY06)

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA \$0

FY05 BA \$0

FY06 BA \$459k

Laboratory Name: Lawrence Livermore National Lab**B&R Code: KC 0203010****FWP/subtask Title under FWP:** Investigations of Electron Correlation in Complex Systems**FWP Number:** SCW0289**Principal Investigator:** Jim Tobin

20c. Purpose: We are developing and using photon dichroic and spin resolved techniques to investigate complex materials and do world-class science. These materials include potential spintronic device sources such as half-metallic ferromagnetic materials and correlated electronic materials such as non-magnetic Ce and δ -Pu, which appears now to have a novel internal spin and orbital polarization in its valence band structure.

20f. Technical Progress:

Sixty years after its discovery, the mystery of the electronic structure of Pu is finally being resolved. In a series of experiments and linked theoretical modeling, the range of possible solutions for Pu electronic structure has been dramatically reduced.

Refereed Journal Publications in calendar year 2006 (also 7 more Conference Proceedings)

1. K.T. Moore, G. van der Laan, J.G. Tobin, B.W. Chung, M.A. Wall and A.J. Schwartz, "Probing the population of the spin-orbit split levels in the actinide 5f states," *Ultramicroscopy* **106**, 261 (2006).
2. S.W. Yu, T. Komesu, B.W. Chung, G.D. Waddill, S.A. Morton, and J.G. Tobin, "f-electron correlations in nonmagnetic Ce studied by means of spin-resolved resonant photoemission," *Phys. Rev. B* **73**, 075116 (2006).
3. J.G. Tobin, S.A. Morton, B.W. Chung, S.W. Yu and G.D. Waddill, "Spin-Resolved Electronic Structure Studies of Non-Magnetic Systems: Possible Observation of the Fano Effect in Polycrystal Ce," *Physica B* **378-380**, 925 (2006).
4. B.W. Chung, A.J. Schwartz, B.B. Ebbinghaus, M.J. Fluss, J.J. Haslam, K.J.M. Blobaum, and J.G. Tobin, "Spectroscopic Signature of Aging in δ -Pu(Ga)," *J. Phys. Soc. Japan* **75**, No. 5, 054710 (2006).
5. Takashi Komesu, G.D. Waddill, and J.G. Tobin, "Spin Polarized Electron Energy Loss Spectroscopy on Fe(100) Thin Films Grown on Ag(100)," *J. Phys. Condensed Matter* **18**, 8829 (2006).
6. J.G. Tobin, "Beyond Spin-Orbit: Probing Electron Correlation in the Pu 5f States," *J. Alloys Compds (JALCOM)*, in press November 2006.
7. J.G. Tobin, S.W. Yu, T. Komesu, B.W. Chung, S.A. Morton, and G.D. Waddill, "Evidence of Dynamical Spin Shielding in Ce from Spin-resolved Photoelectron Spectroscopy," *Europhysics Lett.*, accepted November 2006.

Invited Talks in calendar year 2006:

1. J. G. Tobin, "Determining the Electronic Structure of Pu Using Unorthodox Spectroscopies," Internat'l Workshop on Orbital and Spin Magnetism in Actinides III (IWOSMA3), Lyon, France, June 1-2, 2006.
2. J. G. Tobin, "Determining the Electronic Structure of Pu Using Unorthodox Spectroscopies," Pu Futures Meeting, Asilomar, CA, USA, July 9 -13, 2006.
3. J. G. Tobin, "Determining the Electronic Structure of Pu Using Unorthodox Spectroscopies," International Workshop on the Dual Nature of f-Electrons, Sante Fe, NM, USA, July 16 -18, 2006.

20g. Future accomplishments:

We have developed a new paradigm to explain the electronic structure of Pu, based upon the observation of strong jj-skewed spin orbit splitting and the possibility of spin and orbital polarization in the 5f valence bands of non-magnetic Pu. We are pursuing Double Polarization Photoelectron Dichroism measurements, using spin resolving detection in photoelectron spectroscopy, to test our hypothesis. If successful, we will solve the riddle of Pu electronic structure that has remained unresolved for the last 60 years. We are testing these techniques on Ce, the 4f analog of Pu. (See Pubs 2, 3 and 8.) Interestingly, the results in Pub 8 are the first experimental demonstration of spin or Kondo shielding, using spin polarized photoelectron spectroscopy. It is the proof that the picture proposed by Gunnarsson and Schoenhammer is correct.

20h Relation to Other Projects: Collaborators - USA- National Labs: LBNL- S.A. Morton; USA-Universities: UMR-G.D. Waddill, T. Komesu. International: G. Van der Laan (UK). Both the APS at Argonne National Laboratory and the ALS at Lawrence Berkeley National Laboratory have been used for this work. We interact frequently with the personnel from LANL. (See Invited Talks #2 and #3 for examples.)

Authorized Budget (BA) for FY04, FY05, FY06:**FY04 BA \$341k****FY05 BA \$315k****FY06 BA \$300k**

Laboratory Name: Lawrence Livermore
B&R Code: KC020301

FWP and/or subtask Title under FWP:

Manipulation and Quantitative Interrogation of Nanostructures (Formally Known As: Advanced Heterointerfaces)

FWP Number: SCW0289

Program Scope:

The focus of this research is the quantitative investigation of the effects of size, surface composition, proximity, and dopants on semiconductor nanoparticle properties. We employ unique methods of particle synthesis that allow the greatest control over these physical parameters and utilize state-of-the-art synchrotron radiation-based characterization methods that provide element-specific atomic and electronic structure information. This powerful combination has proven most valuable to the condensed matter theory community who have compared the experimental data to their computation results with and, as a direct result, helped refine our understanding of quantum dot structure/property relationships and guided new material discovery.

Major Program Achievements (over duration of support):

Condensed-phase hydrogen-terminated diamond clusters diamondoids have been studied with soft-x-ray emission and x-ray-absorption spectroscopy. The diamondoids are size- and shape-separated into monodisperse samples, and have perfect hydrogen termination. Soft x-ray emission measurements of the valence band edge show a shift toward lower energy in the diamondoids with decreasing particle size. Solid-state diamondoid x-ray absorption indicates, as reported previously in the gas phase, that the lowest unoccupied states are relatively fixed in energy and dominated by states associated with the hydrogen terminated surface. These results imply an increasing HOMO-LUMO gap with decreasing size, where energy shifting, and by extension quantum confinement, occurs only in the occupied states. These experimental results are compared with theoretical calculations on the electronic structure of diamondoids. We have also successfully measured the change in conduction density of states as a function of particle size and surface termination in CdSe quantum dots, which has been unobserved until now. As the CdSe particle size decreases, s states in the bottom of the conduction band shift to higher energy due to quantum confinement while hybridized states higher in the conduction band are not affected by size. These results suggest that there exists an upper limit to extent the conduction bands of CdSe can shift with particle size and should have impact on the future fabrication of electronic materials based on CdSe. The results have been used to interpret conflicting theories on the size dependent evolution of the conduction band states in CdSe.

Program Impact:

This study offers an unprecedented opportunity within the group IV clusters because we will be able to investigate and understand the evolution of the electronic structure of carbon from methane, through small diamond-like carbon clusters and diamond nanoparticles to bulk diamond. The lowest unoccupied states are overwhelmingly dominated by molecular orbitals associated with the hydrogen surface termination, and thus no band-edge shifts are apparent, contrary to expectations from quantum confinement theory and previous results of group IV semiconductors. Our measurements have confirmed that the quantum confinement effect occur solely in the occupied states of the diamond nanoparticles.

Interactions:

LLNL BES programs: A. Williamson and J. de Yoreo; Chevron Texaco Molecular Diamond Technologies: J. Dahl, B. Carlson; UC-Davis: Subhash Risbud; UC- Santa Cruz: J. Zhang;

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

6 invited talks at major national and international meeting. Chemistry, Material and Life Science Division excellence in publication award. - Meeting Chair for the Fall 2006 Materials Research Society Meeting.

Personnel Commitments for FY2004 to Nearest +/- 10%:

T. van Buuren (staff scientist) 10% Rob Meulenberg (staff scientist) 20% Trevor Willey (staff scientist) 20% , April Montoya Vaverka (student) 100% time this project but only paid for 20% time by DOE

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA \$341k

FY05 BA \$315k

FY06 BA \$300k